con. to EP 0 771 644

3

OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

Ottawa Hull K1A 0C9

(21) (A1) 2,189,319
(22) 1996/10/31
(43) 1997/05/04

(51) Int.Cl.[6] B32B 5/18

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Polyurethane Composites Produced from Recycled Polyols and a Process for Their Production

(72) Rasshofer, Werner - Germany (Federal Republic of) ;
Lammeck, Adolf - Germany (Federal Republic of) ;
Glasder, Andreas - Germany (Federal Republic of) ;

(71) BAYER AKTIENGESELLSCHAFT - Germany (Federal Republic of) ;
BAYERISCHE MOTOREN WERKE AKTIENGESELLSCHAFT - Germany (Federal Republic of) ;

(30) (DE) 195 40 949.3 1995/11/03

(57) 10 Claims

Mo-4557
LeA 31,319

POLYURETHANE COMPOSITES PRODUCED FROM RECYCLED POLYOLS AND A PROCESS FOR THEIR PRODUCTION

ABSTRACT OF THE DISCLOSURE

Composites (sandwich elements) having a polyurethane core and at least one covering layer of a fiber-reinforced plastic material are produced from (a) a polyurethane core which is the reaction product of a polyisocyanate with a polyol composition obtained by chemical decomposition of polyurethane and/or polyurea wastes and having an OH number in the range of from 100 to 500 mg KOH/g, a water content of from 0 to 5 wt.% and a viscosity greater than 2,000 mPa·s (20°C) and (b) at least one covering layer of a plastic material reinforced with natural fibers. These composites are useful in motor vehicle construction, furniture construction, machine construction and the construction of apparatus. They are preferably used in motor vehicle construction, in particular, as moldings in the interior of the motor vehicle.

Mo-4557
LeA 31,319 -US

POLYURETHANE COMPOSITES PRODUCED FROM RECYCLED POLYOLS AND A PROCESS FOR THEIR PRODUCTION

BACKGROUND OF THE INVENTION

The present invention relates to polyurethane composites (sandwich elements) produced from recycled polyols and to processes for their production and use.

Composites having a polyurethane core and fiber-reinforced covering layers made of a different (i.e., non-polyurethane) material are used in a wide variety of applications. Such composites are used, for example, in the production of high-quality structural parts for motor vehicles and motor vehicle body work, particularly in the interior of the motor vehicle. Two basic methods for the production of composite articles of this kind are known in the art -- the filling method and the coating method. In the filling method, two half shells (covering layers) are precast, placed in a mold and the cavity between the shells is filled with a polyurethane (PU) foam. In the known coating construction method, a core made of a PU foam is placed in a mold and coated with a suitable covering material made, for example, of fiber-reinforced plastics such as epoxy resins or unsaturated polyester resins.

Until now, polyol compositions recovered from polyurethane or polyurea wastes (i.e., recycled polyols) have hardly been used in the production of composites having a polyurethane core.

BACKGROUND OF THE INVENTION

It is an object of the present invention to provide high quality composite materials having a polyurethane core in which the polyurethane was produced from recycled polyols.

It is another object of the present invention to provide a process for the production of high quality composite materials having a polyurethane core and an outer layer made of a plastic reinforced with

natural fibers in which the polyurethane core has been produced with a polyol composition recovered from polyurethane and/or polyurea wastes.

These and other objects which will be apparent to those skilled in the art are accomplished by forming a polyurethane core from a reaction mixture composed of a polyisocyanate and a recycled polyol. This recycled polyol is obtained by chemical decomposition of polyurethane and/or polyurea waste. This recycled polyol must have an OH number of from about 100 to about 500 mg KOH/g, a water content of up to 5 wt.% and a viscosity greater than 2,000 mPa·s at 20°C. To this polyurethane core is applied a plastic material which is reinforced with natural fibers.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to composites having a polyurethane core and at least one covering layer of a fiber-reinforced plastic material. The polyurethane core is produced by reacting a polyisocyanate with a polyol composition obtained by chemical decomposition of polyurethane and/or polyurea wastes. The polyol composition has an OH number in the range of from about 100 to about 500 mg KOH/g, a water content of from 0 to 5 wt.% and a viscosity of more than 2,000 mPa·s (20°C). The covering or outer layer is made of a plastic material reinforced with natural fibers.

It is surprising that high-quality polyurethane cores for composite articles can be produced at all using polyol compositions satisfying these requirements because polyols having a far higher OH number (in most cases in the range of from 300 to 1,000) and a considerably lower viscosity (in most cases in the range of <2,000 mPa.s (20°C)) have been used in known processes. The polyol characteristics required for the practice of the present invention may be achieved by adjusting the properties of recycled polyols obtained directly by chemical decomposition of polyurethane and/or polyurea wastes by means of additives described more precisely below.

The composites of the pr sent invention are in the form of sandwich elements which contain, in addition to a polyurethane core formed from a recycled polyol, at least one covering layer made of a plastic material, preferably an epoxy resin or an unsaturated polyester resin, and natural fibers as reinforcement. The covering layer is preferably composed of a fiber-reinforced plastic material. Any of the known fibrous natural fibers, particularly, banana fibers, flax fibers, jute fibers, hemp fibers, sisal fibers and/or coconut fibers in the form of waste fiber, knitted fabric and woven fabric are suitable bonded natural fibers. These fibrous materials may reinforce epoxy-unsaturated polyester resins, polyurethane (PU) resins, melamine resins, vinyl resins or even thermoplastic powders. These binders can be introduced and applied by spraying, rolling, coating with a knife, or pouring. When the preferred PU resins are used, the binders may also contain PU recyclates.

The composites of the present invention are suitably of sandwich construction comprising a covering or coating layer A composed of a plastic material reinforced with natural fibers, a core layer B composed of a polyurethane foam formed from a recycled polyol, and if desired, an additional layer which is either composed of the same material as layer A or composed of a different material. Decorative materials such as films, molded skins, textiles or carpet may then be applied to the outer layer. This application may be conducted in a separate operation or even in a single production step (one-step method) or by pressing behind in known manner (direct coating) directly onto the external surfaces of the covering layer(s). In multilayer sandwich structures, additional layers of different materials may also optionally be included.

Any of the common reaction products of an isocyanate and the commonly used diols and/or polyols (e.g., polyesters or polyethers) may be used as the polyurethane or polyurea wastes which are decomposed

to produce the polyol compounds used in the practice of the present invention.

The present invention also provides a process for the production of composites (sandwich elements) having a polyurethane core and at least one fiber-reinforced covering layer. In this process, a polyisocyanate is reacted with a polyol composition obtained by chemical decomposition of polyurethane and/or polyurea waste and optionally other auxiliary substances and additives. The polyol composition must have an OH number in the range of from about 100 to about 500, preferably from about 200 to about 450, most preferably from about 250 to about 400 mg KOH/g, a water content of from 0 to about 5 wt.%, preferably from about 0.2 to about 2 wt.%, most preferably from about 0.5 to about 1 wt.% and a viscosity at 20°C of more than 2,000 mPa·s, preferably from about 3,000 to about 20,000 mPa·s, most preferably from about 5,000 to about 10,000 mPa·s. At least one covering layer of a plastic material reinforced with natural fibers is applied to the polyurethane core.

In the process of the present invention, any of the known auxiliary substances and additives may be used. Examples of such auxiliary substances and additives include: release agents, blowing agents, fillers, catalysts and flameproofing agents.

The process of the present invention may be carried out by the filling (deposit) method or by the coating method. Both the filling construction and the coating construction methods are known to those skilled in the art. In the filling method, two half shells (for example, covering layers made of a plastic material reinforced with natural fibers) are precast and placed in a mold. The cavity between the shells is filled using the PU foam produced in accordance with the present invention. In the coating construction method, a core made of PU foam produced in accordance with the present invention is placed in the mold and then

coated with a covering material reinforced with natural fibers such as an epoxy resin or polyester resin reinforced with natural fibers.

The composites of the present invention containing a foamed PU core are preferably produced by the coating construction method using recycled polyols. Any of the known conventional blowing agents and auxiliary substances (e.g., release agents) may be added. If no external release agent is added during the production of the composites of the present invention by the coating construction method in a mold, then a particularly strong adhesive bond between the polyurethane core material and the coating material is achieved without any need for finishing or preparing the coating and/or core layer. Any of the known plastic materials reinforced with natural fibers may be used as the coating layer in such a process.

The polyols used in the practice of the present invention may be obtained by chemical decomposition of any polyurethane and/or polyurea wastes. Even the decomposition products of polyurethane and/or polyurea composite materials may be used. These composite materials may be composed of PU and other materials such as thermoplastics. Where the non-PU material is a thermoplastic, the thermoplastic material should be separated from the polyurethane to a large extent before recycling the PU. Such a composite material may be, for example, an automobile control panel made of a glass-fiber reinforced PU support, a soft-textured PU foam as back-filling material or an aliphatic PU skin as a decorative and covering layer.

Methods for chemically decomposing polyurethane and/or polyurea wastes into polyol compounds are known. Examples of such known processes include aminolysis, alcoholysis and glycolysis. These methods have already been described in detail in the prior art. See, for example, W. Raßhofer, Recycling von Polyurethan-Kunststoffen, Hüthig-Verlag, Heidelberg 1994.

The polyol compositions used in the practice of the present invention are preferably obtained by glycolysis of polyurethane and/or polyurea wastes in known manner. Coarsely ground or finely comminuted polyurethane and/or polyurea wastes are reacted at temperatures of from 160 to 240°C with glycols, preferably diethylene glycol, in the weight ratio of waste:glycol of from 10:1 to 1:2, preferably from 5:1 to 1:1. After stirring for from about 0.5 to 10 hours, a liquid product having the following characteristics is obtained: OH number in the range of from 20 to 1,070 mg KOH/g, water content in the range of from 0 to 5 wt.%, viscosity at 20°C of >2,000 mPa·s. At very high OH numbers, the viscosity may also be below 2,000 mPa·s. (20°C).

Since the polyol compositions obtained directly from the chemical decomposition of polyurethane and/or polyurea wastes do not generally satisfy the requirements of a polyol suitable for use in the practice of the present invention, the OH number, water content and/or viscosity of the decomposition product are usually adjusted by incorporating additives. For this purpose, mixtures of known additives such as cross-linking agents, cell stabilizers, flow-promoting agents, release agents, catalysts, blowing agents, etc. are added in amounts which total from about 2 to 50 wt.%, based on the weight of the recycled polyol used. The mixtures of additives generally have an OH number of from 300 to 1,050 mg KOH/g, a viscosity of from 100 to 5,000 mPa·s (at 20°C), a water content of from 0 to 10 wt.% and an acid number of from 0 to 100 mg KOH/g.

It is surprising that polyols satisfying the OH number, water content and viscosity requirements of the present invention that are obtained by chemical decomposition of polyurethane and/or polyurea wastes are suitable at all for the production of high-quality polyurethane composites having a sandwich structure, because generally when new (i.e., non-recycled) polyols are used in such processes, those polyols have considerably higher OH numbers (500 to 1,000). The viscosity of

polyol compounds used in the prior art is also generally considerably lower (mostly in the viscosity range of <2,000 mPa·s (20°C)). It was not therefore to be expected that polyol compositions obtained from polyurethane and/or polyurea wastes could be processed into high quality polyurethane composites notwithstanding their far higher viscosity and their lower OH number (reduced activity).

The polyurethane composites of the present invention are useful for the production of high-quality structural components for a variety of applications. The production of these composites makes it possible to use materials generated from waste in an advantageous manner without sacrificing the mechanical properties of the composite product.

The polyols obtained from the chemical decomposition of polyurethane and/or polyurea wastes can be reacted with any of the known polyisocyanates. Suitable polyisocyanates include: aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates. Such polyisocyanates are described, for example, by W. Siefgen in Justus Liebigs Annalen der Chemie, 362, pages 75 to 136. Useful polyisocyanates include those represented by the general formula

$$Q(NCO)_n$$

in which

n represents 2 to 5, preferably 2 to 3, and

Q represents an aliphatic hydrocarbon radical having from 2 to 18 (preferably 6 to 10) carbon atoms, a cycloaliphatic hydrocarbon radical having from 4 to 15 (preferably 5 to 10) carbon atoms, or an aromatic hydrocarbon radical having from 6 to 15 (preferably 6 to 13) carbon atoms.

Examples of such polyisocyanates are given in German Offenlegungsschrift 2,832,253, pages 10 to 11.

Particularly preferred are the commercially available polyisocyanates such as 2,4- and 2,6-toluene diisocyanate, and any mixtures of these isomers ("TDI"); diphenylmethane diisocyanate ("MDI") and polyphenylpolymethylene polyisocyanates which are prepared by aniline-formaldehyde condensation and subsequent phosgenation; as well as polyisocyanates possessing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"). Modified polyisocyanates which are derived from 2,4- and 2,6-toluene diisocyanate or 4,4'- and/or 2,4'-diphenylmethane diisocyanate are particularly preferred.

The polyurethane composites (sandwich elements) of the present invention are useful in motor vehicle construction, furniture construction, machine construction and the construction of apparatus. These polyurethane composites are advantageously used in motor vehicle construction, particularly in the interior of the motor vehicle. In addition to possessing low weight with high strength, the sandwich elements of the composites of the present invention have a particularly low content of emittable and extractable substances. In the motor vehicle sector, these composites can be employed, for example, as two- and/or three-dimensional moldings such as concealable panels or coverings, inside door panels, control panel supports, dashboard supports, air ducts, cable coverings, cable ducts and luggage boot linings. They can also be processed to form housings and covers for housings, pallets, supports for light loads, coverings, vertical and horizontal structural components, bulkhead walls, inlaid floors, et cetera. In the furniture sector, the polyurethane composites of the present invention can also be used as a substitute for tropical wood, particularly in the form of imitation plywood.

The following Examples are intended to illustrate the invention without, however, limiting the scope thereof.

EXAMPLES

Example 1 (Chemical decomposition of polyurethane wastes by glycolysis)

A granular material having a maximum particle size of 8 mm and composed of glass-fiber reinforced polyurethane urea having a density of 1.26 g/cm^3 was subjected to glycolysis. 4 kg of diethylene glycol were placed in a 20 l vessel equipped with stirrer and heating jacket, covered with nitrogen and preheated to 220°C. 8 kg of granulated polyurethane urea were introduced in portions into the hot mixture under a layer of nitrogen. The addition was carried out at a rate such that at any time a stirrable mixture was present. When addition of the granular material was complete, the mixture was stirred at 200-210°C for a period of 90 min, cooled to 160°C, then mixed with 0.2 kg of ethyl acetoacetate and stirred at this temperature for one hour. A liquid product composed of recycled polyols was obtained, which on standing formed two phases. The product had the following properties:

OH number = 353 mg KOH/g
NH number = 33 mg KOH/g
Acid number = 0.07 mg KOH/g
Viscosity = approx. 20,000 mPa·s (20°C)

Example 2 (Production of a foamed polyurethane core for a composite in accordance with the present invention)

To the recycled polyols obtained by glycolysis in Example 1 was added a mixture of additives. This mixture of additives was used in an amount which was 25 wt.%, based on the total weight of polyol. The mixture of additives had the following properties:

OH number = 400 mg KOH/g
Water content = 2.6 wt.%
Viscosity = 1,500 mPa·s (20°C)

The resultant polyol formulation had the following properties:
OH numb r = approximately 380 mg KOH/g
Water content = approximately 1 wt.%
Viscosity = approximately 3,500 mPa·s (20°C)

This polyol formulation was reaction injected molded with polyisocyanate (crude MDI) in known manner to produce a foamed polyurethane molding. An external release agent was not used. A polyurethane molding having a bulk density of 400 kg/m^3 was obtained.

Example 3 (Production of a composite (sandwich element) in accordance with the present invention)

Example 3a

Outside the mold, coconut fiber mats having a substance weight of 600 g/m^2 were impregnated and coated with a PU matrix material (commercially available under the name Baypreg® from Bayer AG) by spraying in known manner.

A mold (steel, 120°C, 300 x 300 x 8 mm) was covered with a covering coconut fiber reinforced PU layer produced as described above, a polyurethane core produced as described in Example 2 and an additional covering layer of the coconut fiber reinforced PU. The mold was then closed. After 2 minutes at 120°C and a pressure of 50 bar, a sandwich element bonded by adhesion was released.

Example 3b

A composite was produced in the same manner as described in Example 3a) with the exception that a decorative film of PVC/ABS was laid onto one of the covering layers before the mold was closed. After 2 minutes at 120°C and at a pressure of 50 bar, a sandwich element

bonded by adhesion and having an additional decorative layer was released.

All sandwich elements produced in accordance with the present invention exhibited a very good adhesive bonding between core and covering layer, good dimensional stability and strength.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A composite comprising a polyurethane core and at least one outer layer in which

a) the polyurethane core is the reaction product of

1) a polyisocyanate

with

2) a polyol obtained by chemical decomposition of polyurethane and/or polyurea waste which has an OH number of from about 100 to about 500 mg KOH/g, a water content of up to 5 wt.% and a viscosity greater than 2,000 mPa·s at 20°C

and

b) the outer layer is a plastic material which is reinforced with natural fibers.

2. The composite of Claim 1 in which the outer layer is a plastic which is reinforced with fibers selected from banana fibers, flax fibers, jute fibers, hemp fibers, sisal fibers, coconut fibers and combinations of these fibers.

3. The composite of Claim 2 in which the plastic of the outer layer is polyurethane.

4. The composite of Claim 3 in which the polyurethane core is foamed polyurethane.

5. The composite of Claim 2 in which the polyurethane core is foamed polyurethane.

6. The composite of Claim 1 in which the plastic of the outer layer is polyurethane.

7. The composite of Claim 1 in which the polyurethane core is foamed polyurethane.

8. The composite of Claim 1 in which the polyol used to produce the polyurethane core is obtained by glycolysis of polyurethane and/or polyurea waste.

9. A process for the production of the composite of Claim 1 comprising coating the polyurethane core with the plastic reinforced with natural fibers which forms the outer layer.

10. The process of Claim 9 in which the polyol used to produce the polyurethane core is obtained by glycolysis of polyurethane and/or polyurea waste.